

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the paper carton suitable for being filled up with liquid contents. It is related with the paper carton which consists of a layered product of the resin layer and paper containing the layer of the polyamide resin generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid in more detail.

[0002]

[Description of the Prior Art] The paper carton which consists of a layered product of the former to paper and a resin layer is widely used as a container of liquefied objects, such as fruit juice, an alcoholic beverage, oil, and a detergent, from advantages, like a lightweight thing, that it can collect and reuse after use, and there is comparatively little calorific value at the time of incineration. The paper carton which carried out the laminating of the various resin layers is proposed from the cutoff nature (it being called gas barrier - nature) of gases, such as oxygen and a steam, the shelf life of the flavor of contents, etc. changing with classes of resin layer which carries out the laminating of the paper carton which consists of a layered product of paper and a resin layer.

[0003] Having the property which the layer of the polyamide resin generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid in these resin layers was excellent in gas barrier - nature, and was [be / even if it heats for heat adhesion / little generation of a harmful decomposition product] excellent when contents' oxidizing and being unable to deteriorate easily and thermal stability were good and fabricated a layered product in a container is known. For this reason, the paper cartons (JP,53-119984,A, JP,3-49953,A, etc.) which consist of a layered product of the resin layer and paper containing XD-6 structural unit, or the paper carton (JP,6-305086,A) which consists of a layered product with the paper which combined the polyamide resin layer of the class of further others is proposed. However, it is easy to generate a crack minute on paper at the process which will attach the so-called ruled line for bending in the configuration of a container from a layered product if a paper carton is manufactured according to these proposals, and if the obtained paper carton is filled up with contents and it saves in ordinary temperature for one to two weeks, a container will deform, an appearance will get worse remarkably and commodity value will fall. This phenomenon is considered that the mechanical property and absorptivity of resin which are generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid are related.

[0004]

[Problem(s) to be Solved by the Invention] The place made into the purpose of this invention has good workability, and even if saved in the condition of having been filled up with contents, it is obtaining the paper carton with which change of a gestalt consists of a layered product of the polyamide resin layer and paper which are generated at the polycondensation reaction of few good meta-xylylene diamines and adipic acids of an appearance.

[0005]

[Means for Solving the Problem] In the paper carton which consists of a layered product of the resin layer and paper which contain the layer of the polyamide resin generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid as a result of this invention persons' examining the above-mentioned purpose wholeheartedly The rigidity of 0.60 - 0.95 g/cm³ and a longitudinal direction

finds out being attained with the paper carton characterized by being per [0.40] micrometer in thickness - 0.90 gf-cm, and the consistency of paper came to complete this invention.

[0006]

[Embodiment of the Invention] The paper carton of this invention consists of a layered product of the resin layer and paper containing the layer of the polyamide resin generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid.

[0007] In this invention, the polyamide resin generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid What consists of a structural unit which all the resin generates at the polycondensation reaction of meta-xylylene diamine and an adipic acid, What consists of a structural unit which makes meta-xylylene diamine a subject and is generated at the polycondensation reaction of the PARAKI silylene diamine of a small amount, and an adipic acid (The structural unit which makes a subject hereafter the structural unit or meta-xylylene diamine generated at the polycondensation reaction of meta-xylylene diamine and an adipic acid, and is generated at the polycondensation reaction of the PARAKI silylene diamine of a small amount and an adipic acid may be called XD-6 structural unit.) Or the polyamide resin which made the subject m- and/or p-xylylene diamine and an adipic acid, and copolymerized other diamines or dicarboxylic acid in it is said. As an example of the diamine in which these copolymerization is possible, ethylenediamine, a tetramethylenediamine, pentamethylene diamine, a hexamethylenediamine, octamethylene diamine, octamethylene diamine, etc. are mentioned. Moreover, as an example of the dicarboxylic acid in which these copolymerization is possible, a sebacic acid, cork acid, a glutaric acid, an azelaic acid, etc. are mentioned. In the case of copolymerization polyamide resin, in order to maintain the gas barrier - nature of resin, and crystallinity moderately, it is desirable that the content of XD-6 structural unit is more than 60 mol %.

[0008] moreover, the layer of the polyamide resin containing XD-6 structural unit -- XD-6 structural unit -- more than 90 mol % -- other polyamide resin may be mixed to the polyamide resin which it has, and nylon 6, Nylon 66, Nylon 46, Nylon 610, Nylon 12, etc. are mentioned to it as an example of other polyamide resin to mix. Depending on a request, little mixing of resin other than a polyamide, for example, polyethylene, an ethylene-vinylalcohol copolymer, an ethylene-acrylic-acid copolymer, an ethylene-maleic-anhydride copolymer, polyester, the polycarbonate, etc. can be carried out further again. in order not to reduce gas barrier - nature too much in the case of the mixture of resin -- XD-6 structural unit -- more than 90 mol % -- it is desirable that the polyamide resin which it has contains 60% of the weight or more.

[0009] Although the resin layer in this invention may be a monolayer or you may be a multilayer thing more than two-layer, at least one of them needs to be polyamide resin which has XD-6 structural unit. The resin layer which compounded the layer of other resin with the layer of the polyamide resin containing XD-6 structural unit is sufficient. As an example of the resin compounded with the layer of the polyamide resin which has XD-6 structural unit, polyester, such as polyethylene, polypropylene, polyvinyl alcohol, an ethylene-vinylalcohol copolymer, a polyvinylidene chloride, polystyrene, and polyethylene terephthalate, a polycarbonate, etc. may be mentioned, and a thing, or non-extended one shaft or the thing which has carried out biaxial extension is sufficient as the layer of these resin. Although the thickness of a resin layer is based also on the class of contents of a paper carton, and a property, its 5-40 micrometers are desirable.

[0010] Moreover, metal layers, such as an aluminum foil and tinfoil, can also be compounded with these resin layers for the purpose of grant of protection-from-light nature, or much more improvement in gas

barrier - nature. Although it can be prepared in the location of the arbitration of the layered product which constitutes the container of this invention, when the layer of the polyamide resin which has XD-6 structural unit in this invention is changed into the condition of a container, preparing inside paper is desirable and it is still more desirable to prepare between the layers of heat-sealing nature resin, such as low density polyethylene suitable for the heat adhesion when fabricating paper and a container, straight chain polyethylene, low consistency straight chain polyethylene, and polypropylene.

[0011] If the paper which constitutes the layered product in this invention mills a natural fiber, synthetic fibers, or such mixture and it is obtained, there will be especially no limit and animal fibers, such as a vegetable fiber which pulped wood fiber, such as softwood pulp and hardwood pulp, cotton yarn, the sugarcane, the bamboo, etc., wool, and silk thread, etc. will be mentioned as a natural fiber used for paper milling. Moreover, as a synthetic fiber, polyethylene, polypropylene, polyester, a polyamide, cellulose acetate, etc. are mentioned. In the paper obtained from these fiber, what was obtained from the field of the mechanical property of paper and a thermal property by wood pulp is desirable, and especially the thing by which the point that tensile strength becomes high to softwood pulp was milled from the wood pulp which occupies 40% of the weight or more of all pulp by dryness is desirable.

[0012] Moreover, as for the paper used in this invention, it is desirable to make the under coat agent of an olefin system, a polyethyleneimine system, an isocyanate system, a polyester system, a polyurethane system, and a vinyl system contain at the time of paper milling of paper, or to be applied on the surface of paper after paper milling in order to raise an adhesive property with a resin layer. A polyethyleneimine system under coat agent is preferably used in these under coat agents. the paper used in this invention -- the consistency -- 0.60 - 0.95 g/cm³ it is -- things -- required -- especially -- 0.65 - 0.90 g/cm³ It is desirable. The consistencies of paper are 0.60 g/cm³. When not filling, it is easy to generate a minute crack on paper at the process which attaches the ruled line for bending in the configuration of a container from a layered product, and the production yield of a good paper carton falls remarkably. Since this has the comparatively high elastic modulus of the layer of the polyamide resin containing XD-6 structural unit, it is considered in other resin that the height of a ruled line originates in it being necessary to make it higher than the case where a laminating is carried out. Since the elastic modulus of the layer of the polyamide resin which it is hard to bend the paper itself and contains XD-6 structural unit is high when the consistency of paper exceeds 0.95 g/cm³, bending which met the ruled line becomes difficult and the configuration of the obtained container becomes a defect. In addition, this invention is defined as the consistency of paper being also at the value measured according to "the consistency and test method" of paper and the paper board of JISP1118.

[0013] Furthermore, the rigidity of the longitudinal direction of the paper used in this invention needs to be per [0.40] micrometer in thickness - 0.90 gf-cm, and is 0.45 - 0.80 gf-cm preferably. The longitudinal direction of paper means the longitudinal direction at the time of milling paper here. Usually, when using paper for containers, it is used so that it may become the horizontal direction and parallel whose longitudinal direction of paper receives the gravity of contents. when the rigidity of the longitudinal direction of paper be [thickness] less than 0.40 gf-cm per micrometer, for example, if it be fill up with contents with many rates to the obtained carton-like paper carton that moisture, such as fruit juice and an alcoholic beverage, occupy and save in an ordinary temperature for one to two weeks, the bending section of four square shapes of the horizontal cross section of a container drum section will deform into a circle configuration, it will be blister by the lower part of a container, and an appearance will fall remarkably. Moreover, the rigidity of the longitudinal direction of paper needs to make the

height of a ruled line remarkably high at the process which will attach the ruled line for bending in the configuration of a container from a layered product if thickness exceeds 0.90 gf-cm per micrometer, for this reason destruction (pinhole) of the minute part of a resin layer occurs, gas barrier - nature falls, and they are a lifting and a cone about degradation of contents. In addition, this invention is defined as the rigidity of paper being also at the value which measured according to the "rigidity test method of the paper board by the load bending approach" of JISP8125, and was converted into per micrometer.

[0014] As an approach of obtaining the layered product of a resin layer and paper, an urethane system, acrylic, How to carry out dry laminate of between the layers of each resin which forms the resin layer made into the shape of a film in advance using adhesives, such as a polyester system, and a resin layer, and the paper, How to sandwich and laminate what fabricated in advance the layer of the resin which constitutes a resin layer in the shape of a film, The approach which laminates by carrying out multilayer melting extrusion in coincidence using the approach, two or more extruders, and Phi-DOBUROKKU which carry out the extrusion lamination of the resin which forms a resin layer one by one, Or the approach which combined suitably a sand lamination, dry laminate, and a melting extrusion lamination can be used.

[0015] Furthermore, between the layers of each resin which forms a resin layer, in order to raise the adhesive property between a resin layer and paper, the layer of adhesive high resin can be prepared or physical scientific processing of corona treatment, plasma treatment, ozonization, etc. can be carried out to in process [to laminate] or beforehand. As adhesive high resin, a polyethylene, ethylene-vinylacetate copolymer, maleic-anhydride denaturation ethylene-vinylacetate copolymer, maleic-anhydride denaturation polyethylene, and ethylene-methyl-acrylate copolymer, an ethylene-methacrylic acid methyl copolymer, maleic-anhydride denaturation polypropylene, an ionomer copolymer, etc. are mentioned.

[0016] From the layered product of the resin layer and paper containing at least one layer of layers of the polyamide resin which has XD-6 structural unit acquired in this way The process pierced in the condition of having developed the purpose container, the process which attaches a ruled line, the process which bends a part for jointing of a drum section outside so that the cross section of paper may not contact contents depending on the need (skive processing), The target paper carton can be obtained through the usual container production processes, such as a process which fabricates the process and pars basilaris ossis occipitalis which paste up a drum section, and a head.

[0017] The paper carton of this invention obtained by the above can be suitably used as various forms, the carton of size, a cup, and containers, such as edible oil, such as milk beverages, such as fruit juice, cow's milk, and yogurt, an alcoholic beverage, mineral water, and salad oil, an industrial oil, and a detergent.

[0018]

[Example] Hereafter, although concrete explanation of this invention is further given according to an example, this invention is not limited to these examples. In addition, the measuring method of each physical properties given in an example and the example of a comparison is as follows.

[0019] (1) In the paper carton of the configuration where the four square shape telescopic drum section by which the deformation pars basilaris ossis occipitalis and the upper part of a container were sealed was stood, to the horizontal direction and the flat surface correctly stood to it perpendicularly, after a part of 4 square-shape telescopic part of a container had touched lightly, the container was placed so that one side of the topmost part of 4 square-shape telescopic part might become parallel to a perpendicular

flat surface, and the distance of said parallel lines and perpendicular flat surface was measured. If the lower part of 4 square-shape telescopic part swells (*****) and a container deforms in the manufacture process of a container while filling up with and saving contents in the container, when the bending nature of 4 square-shape telescopic part is poor, this measured value will become large. In addition, this value used the thing 10mm or more as the poor gestalt container.

(2) About 100 surface-discontinuity containers, the suspension (Red check liquid) which will be colored if there is surface discontinuity accompanying the minute crack of paper was applied to the four bending sections of 4 angle system cylinder part of each container, the number of a defect was observed in them, and it expressed in them as the number per 100 containers. In addition, this value used ten or more pieces as the defect container.

(3) Warm water of 65 degrees C of gas cutoff nature of a container was saved in ordinary temperature for after [restoration] three weeks, when each field of the four square shape telescopic upper part of a container was perpendicular, the case where it was curving inside a container was made into gas cutoff ****, and the case where each field of the four square shape telescopic upper part was curving on the container outside was made into poor gas cutoff nature. After being filled up with warm water, if it is made ordinary temperature, the inside of a container will be decompressed, when the gas cutoff nature of a container is good, each field of the four square shape telescopic upper part curves inside a perpendicular or a container, and, as for the case of poor gas cutoff nature, each field curves on the container outside.

(4) 1g of relative viscosity resin of resin was dissolved in 100ml of sulfuric acids 96%, and it is the value which measured solution viscosity at 25 degrees C, and computed from the degree type.

Relative viscosity = the number of fall seconds of the number of fall seconds / sulfuric acid of a resin
 sulfuric-acid solution [0020] The co-extrusion laminator equipped with the extruder, Phi-DOBUROKKU, and the T die of example 1 plurality is used. Consist of 90 % of the weight of softwood pulp, and 10 % of the weight of hardwood pulp, and basis-weight 405 g/m², a consistency 0.75, and the rigidity of a longitudinal direction, carrying out corona treatment to the field of paper whose thickness is 0.72 gf-cm per micrometer 10 micrometers of polyamide resin of the relative viscosity 3.6 compounded from m-xylylene diamine containing some p-xylylene diamine, and an adipic acid, Denaturation polyolefine "Modic F23OOK" (Mitsubishi Chemical make) 10 micrometers, Low density polyethylene "the nova tech L300" (Mitsubishi Chemical make) The resin by which the laminating was carried out to 60-micrometer order within the T die was laminated so that the layer of the polyamide resin which consists only of XD-6 structural unit might touch paper. Furthermore, low-density-polyethylene "nova tech L300" (Mitsubishi Chemical make) 20micrometer was extruded and laminated in the opposite side of the paper which carried out [above-mentioned] the lamination, and the layered product was obtained. After piercing and making a layered product into the shape of a sleeve from the aforementioned layered product through each process of heat adhesion of the drum section by ruled line attachment, skive, and flame heating, each telescopic side of four square shapes filled up with 1.8l. warm water [65-degree C] using the plastic filling machine for alcohol obtained 85cm, and height obtained the paper carton of roofing [upper part] (gable top mold) 25.7cm. Where the paper carton with which it filled up with water is stood, after saving for three weeks, observation, measurement of the deformation of a paper carton, and evaluation of gas cutoff nature were carried out for the number of surface discontinuity. A result is shown in Table 1.

[0021] Each telescopic side of four square shapes where example of comparison 1 basis weight of 420g/

m2, a consistency 0.55, and the rigidity of a longitudinal direction were filled up with 1.8l. water obtained 85cm like the example 1 except thickness using the paper which is 0.57 gf-cm per micrometer, and height obtained the paper carton of roofing [upper part] (gable top mold) 25.7cm. An evaluation result is shown in Table 1.

[0022] It consists of 70 % of the weight of example 2 softwood pulp, and 30 % of the weight of hardwood pulp. Basis-weight 310 g/m2 which applied beforehand the polyethyleneimine system under coat agent "DIKKU dry AC108" (Dainippon Ink & Chemicals make) in gravure, A consistency 0.82 and the rigidity of a longitudinal direction use [thickness] the paper which are 0.65gf(s)9 and cm per micrometer. Moreover, it is made to be the same as that of an example 1 except using the mixed polyamide resin of 70 % of the weight of polyamide resin, and 30 % of the weight of Nylon 66 resin of relative viscosity 3.3 used in the example 1 as polyamide resin. Each telescopic side of four square shapes filled up with 1.0l. warm water obtained 7cm, and height obtained the paper carton of roofing [upper part] (gable top mold) 19.5cm. An evaluation result is shown in Table 1.

[0023] Basis-weight 315 g/m2 which consisted only of example of comparison 2 hardwood pulp, and applied beforehand the polyethyleneimine system under coat agent "DIKKU dry AC108" (Dainippon Ink & Chemicals make) in gravure, each telescopic side of four square shapes where a consistency 0.78 and the rigidity of a longitudinal direction were filled up with 1.0l. water like the example 2 except using the paper whose thickness is 0.35 gf-cm per micrometer came out, and the upper part obtained the roofing (gable top mold) paper carton. An evaluation result is shown in Table 1.

[0024] The laminator with which the extruder of example 3 plurality, an extrusion lamination, and Sandra Mine-TO were respectively equipped with the possible mouthpiece is used. Consist of 80 % of the weight of softwood pulp, and 20 % of the weight of hardwood pulp, and basis-weight 430 g/m2, a consistency 0.79, and the rigidity of a longitudinal direction, carrying out corona treatment to the field of paper whose thickness is 0.63 gf-cm per micrometer Beforehand low density polyethylene on one side 15 micrometers, Low density polyethylene "*** TOROSEN 204" (TOSOH make) is used for an opposite side for the field which carried out 15-micrometer laminating of the low density polyethylene of the film which consists of mixture of 70 % of the weight of resin, and 30 % of the weight of Nylon 66 resin which consists only of XD-6 structural unit which carried out the laminating of the 60 micrometers. He is Sandra Mine in 15 micrometers in thickness. - TO was carried out. It pulled, low-density-polyethylene "*** TOROSEN 204" (TOSOH make) 20micrometer was extruded and laminated in the opposite side of *****, and the layered product of a resin layer and paper was obtained. The upper part obtained the roofing (gable top mold) paper carton by telescopic [of four square shapes filled up with 1.8l. water] like the example 1 using this layered product. An evaluation result is shown in Table 1.

[0025]

[Table 1]

表 1

	坪量 g/m^2	密度 g/cm^3	こわさ $\text{gf}\cdot\text{cm}$	表面欠陥 コ/器100本	容器変形量 mm	気体の 遮断性
実施例 1	405	0.75	0.72	0	4	良
比較例 1	420	0.55	0.57	26	16	不良
実施例 2	310	0.82	0.65	0	6	良
比較例 2	315	0.78	0.35	10	15	不良
実施例 3	430	0.79	0.63	1	5	良

[0026] It turns out that surface discontinuity and deformation occur and the paper carton of the invention in this application cannot obtain a good paper carton if a consistency (example 1 of a comparison) and the rigidity (example 2 of a comparison) of a longitudinal direction separate from the range of this invention to surface discontinuity and deformation showing the engine performance which was excellent few so that clearly from the result of Table 1.

[0027]

[Effect of the Invention] Even if it is filled up with a liquid drink, oil, etc. and being saved for a long period of time, the paper carton of this invention does not have degradation of contents, and deterioration, moreover, its appearance of a container is good and troubles -- it is hard to take out according to deformation from a showcase -- do not generate it.